Chapter 9

Recent Advances in Electrocatalytic Applications of Ionic Liquids

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Additional information is available at the end of the chapter

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Abstract

Ionic liquids have emerged as an environmentally friendly alternative to the volatile organic solvents. Being designer solvents, they can be modulated to suit the reaction conditions, therefore earning the name "task-specific ionic liquids." Though primarily used as solvents, they are now finding applications in various fields such as catalysis, electrochemistry, spectroscopy, and material science to mention a few. The goal of this chapter is focused on the electrocatalytic applications of ionic liquids, which can be used as catalysts and catalytic supports in electrochemistry. Their scope has marched beyond academic research laboratories to industries where their practical applications have been leading to various sustainable technologies. Flexibility to modulate properties by changing design endows freedom to a chemist to design an ionic liquid according to one's own requirement. To conclude, it can be said that the field of ionic liquid electrocatalysis holds enormous possibilities to be explored.

Keywords: ionic liquid, electrochemistry, electrocatalysis, sensors, electrodeposition, electroredox, application

1. Introduction

Ionic liquids (ILs) are organic salts remaining liquid even under ambient temperatures [1]. They consist of organic cations (e.g., imidazolium, pyridinium, pyrrolidinium, phosphonium, ammonium) and organic/inorganic anions with side chains of alkyl or different functional groups and aromatic moieties (e.g., trifluoromethanesulfonate, bis(trifluoromethyl)sulfonyl imide) [2, 3]. Characteristic interesting properties of these liquid salts include good thermal stability, wide liquid temperature range, considerable ionic conductivity, a broad electrochem-

ical window, and a wide solubility and miscibility range [4, 5]. Due to these advantages, they have been considered as environmental benign solvents compared to volatile organic solvents and "green designer solvents." As a result, ILs are widely used in various chemical transformations such as electrocatalysis, electrosynthesis, electrodeposition, electrochemical capacitor, and lithium batteries (**Figure 1**) [6]. Nowadays, ionic liquids are of immensely growing importance for the electrochemical technology [7–9]. The applications of ILs reveal new perspectives in electrocatalysis and other branches of applied electrochemistry [10–12].

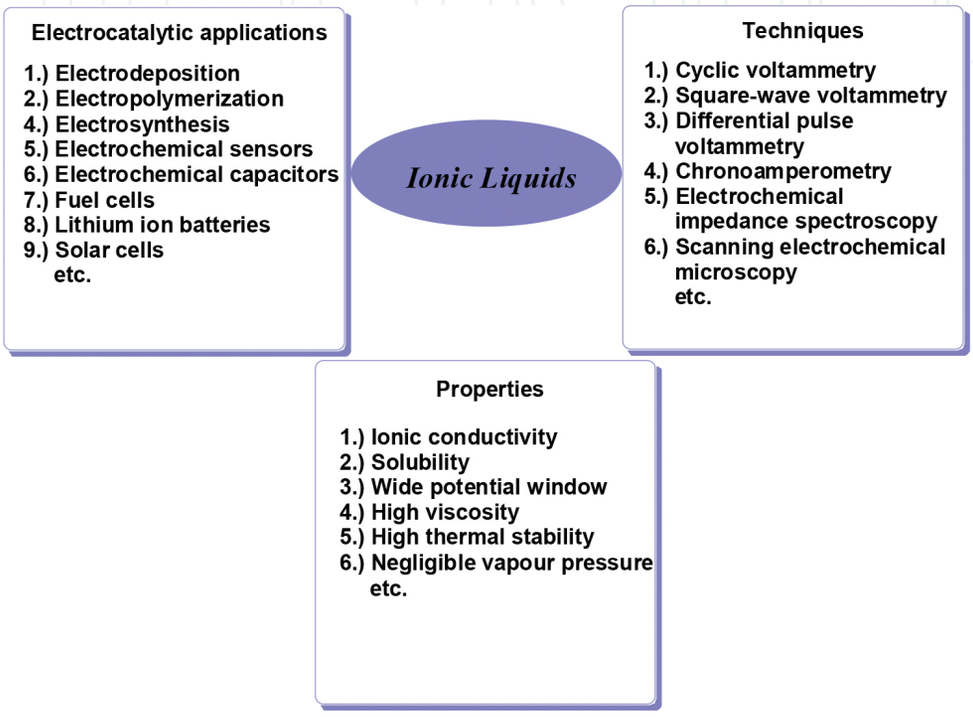

Figure 1. Schematic representation of the general properties of ILs, electrochemical techniques, and electrochemical applications of ILs.

Electrocatalysis is a special type of catalysis that speeds up the rate of an electrochemical reaction occurring on electrode surfaces or at liquid/solid interfaces [13]. In this chapter, we mainly overviewed recent advances in electrocatalytic applications of ionic liquids such as electrosensing, electrodeposition, electroredox, and electropolymerization.

2. Electrochemical applications of ionic liquids

2.1. Electrochemical sensors

Nonenzymatic amperometric sensor for direct determination of some electroactive molecules is an attractive alternative technique to solve the disadvantages of enzymatic biosensors [14]. They have received continuously increasing interest in the recent years [15, 16]. ILs are used primarily as modifying materials of electrodes (IL can interact with other materials to get

composites which exhibit the synergistic effects [17]) for the fabrication of sensors due to their performance of achieving electron transfer (DET) directly. The modified electrodes in electroanalysis offer several advantages. They can not only lower the overpotential but also increase the reaction rate and sensitivity and improve selectivity. These advantages have been evidenced by numerous experiments.

Rahman et al. [18] reported the synthesis of ionic liquid [ClPr]NTf_2 by simple metathesis reaction at room temperature (**Figure 2**). The [ClPr]NTf_2 can fabricate the chemical sensor with conducting coating binders onto glassy carbon electrodes, which showed high selective and sensitivity on sensing applications. The performances of the fabricated sensors are excellent in terms of selectivity, sensitivity, detection limit, etc. This novel approach was introduced a well-organized route of efficient chemical sensor development for environmental pollutants and health-care fields in broad scales.

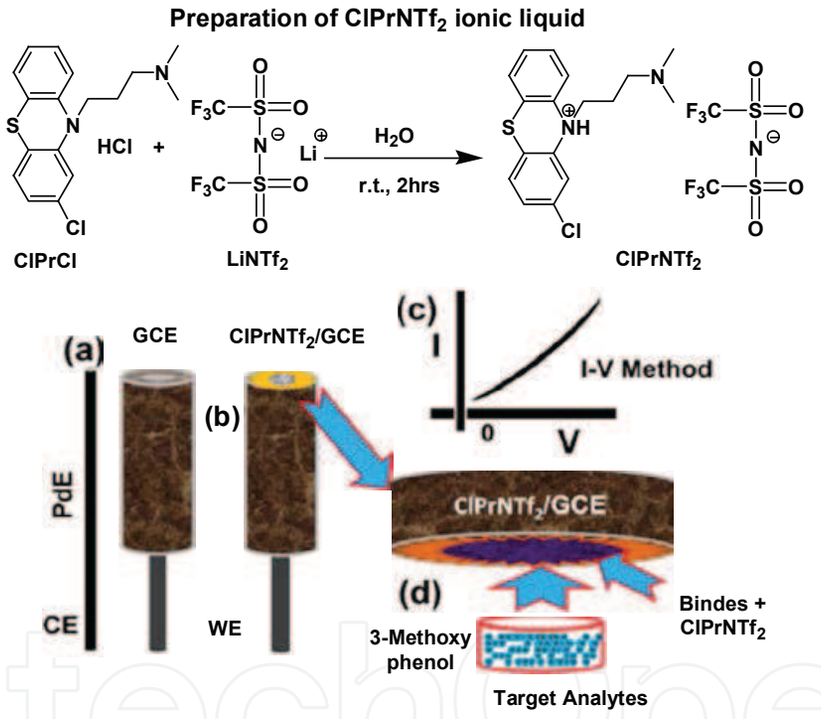

Figure 2. Preparation of ClPrNTf2 and the mechanism of sensor development. (a) ClPrNTf2 coated GCE with conducting coating binders, (b) detection I-V method (theo-retical), (c) observed I-V responses by ClPrNTf2/GCE, and (d) proposed adsorption mechanisms of 3-methoxy phenol detection in presence of ClPrNTf2 onto GCE.

Atta et al. [19] fabricated reduced cyclodextrin/ionic liquid crystal/graphene composite electrode for the determination of some neurotransmitters such as dopamine (DA), epinephrine (EP), and norepinephrine (NEP) (**Figure 3**). Besides the pre-concentrating effect of CD, this electrode expected large graphene surface area, good electron mobility, and high ionic stability and conductivity of ionic liquid. Optimization of the sensor performance was presented and resulted in a better current signal. The sensor was sensitive and successfully applied for direct determination of EP in human urine samples with good recovery results.

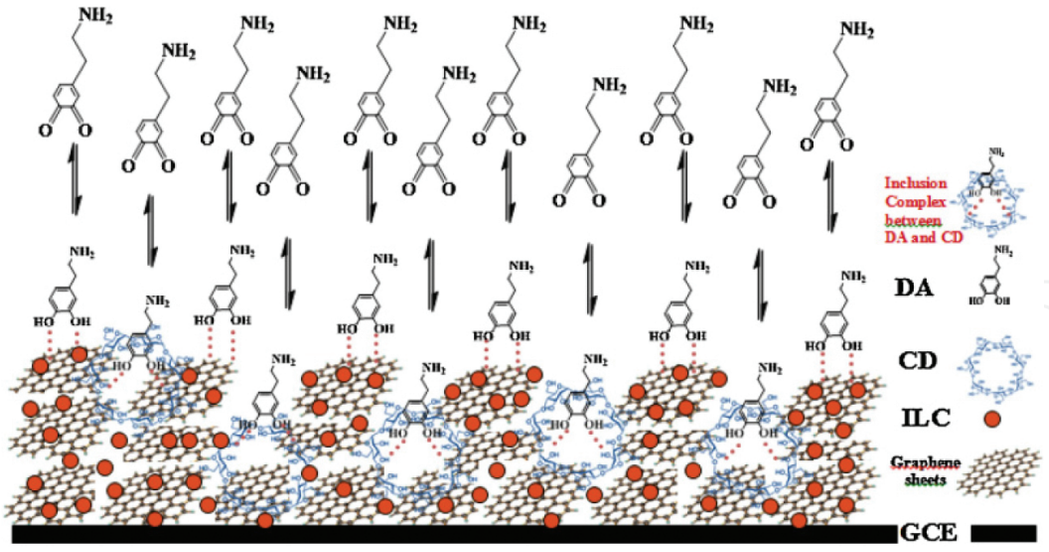

Figure 3. Schematic representation of the proposed sensor with the inclusion complex between the studied compounds and CD.

Yu et al. [20] fabricated an ionic liquid-Fe_3O_4 nanoparticle-graphite composite electrode (IL-Fe_3O_4NPs-GP) (**Figure 4**). A hydrophobic ionic liquid BMP-TFSA was used to combine Fe_3O_4NPs and graphene paper (GP) and to substitute paraffin oil that is conventionally used as the organic binder for preparing carbon-paste electrodes. The electrode showed good stability and the synergistic effect from the combination of IL and Fe_3O_4NPs, exhibiting a high sensitivity but a narrower dynamic range with a detection limit of 0.5 lM.

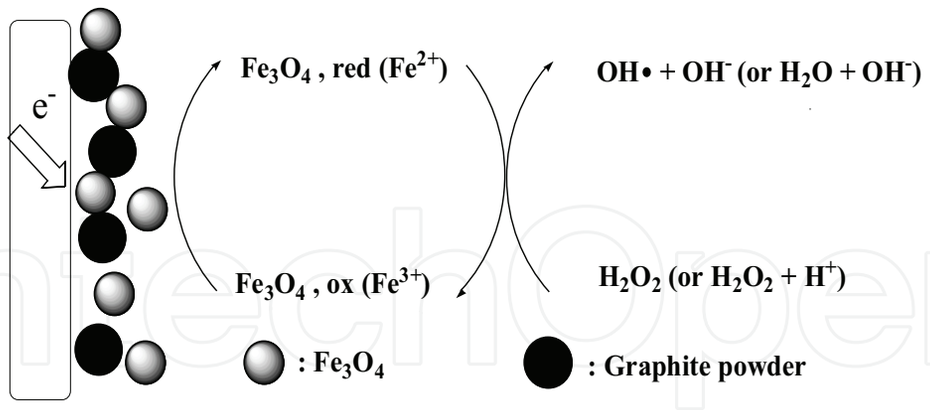

Figure 4. IL-Fe_3O_4NPs-GP electrode for detection of H_2O_2.

He et al. [21] reported the synthetic method for the free-standing GP-supported graphene-CNT-IL nanocomposite graphene-CNT-IL/GP (**Figure 5**), which was formulated by blending three-dimensional porous graphene-carbon nanotube (CNT) assembly with ionic liquid on two-dimensional graphene paper (GP). The results showed that the graphene-CNT-IL/GP exhibited excellent sensing characteristics in terms of selectivity, reproducibility, and sensitivity in electrochemical detection of glucose.

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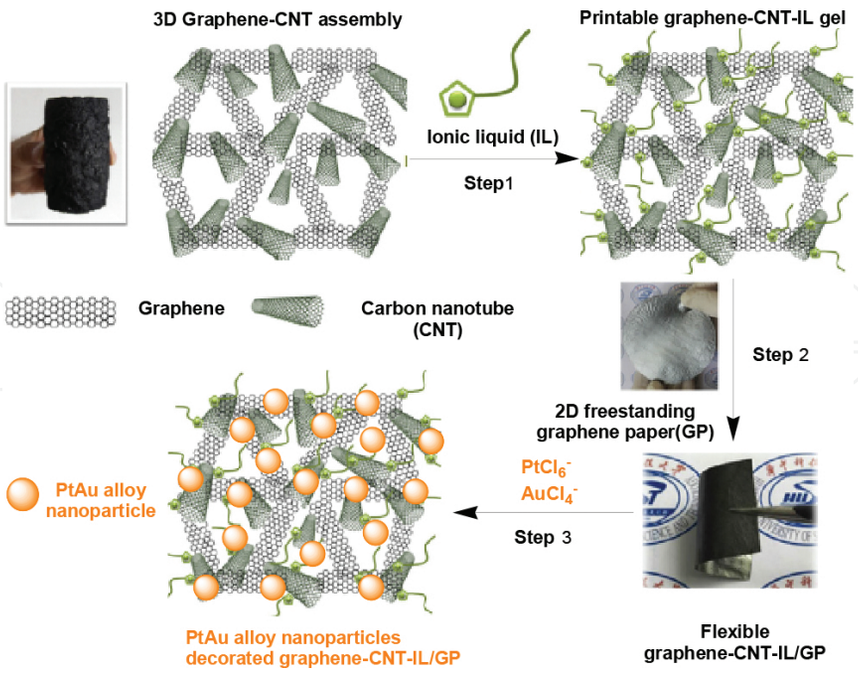

Figure 5. Preparation process of PtAu alloy nanoparticle decorated graphene-CNT-IL/GP.

Okuzaki et al. [22] synthesized the transparent ionic liquid/polyurethane (IL/PU) gels firstly (**Figure 6**). They observed that with increasing the IL content from 0 wt% to 40 wt%, both ionic conductivity and electric-double-layer capacitance increased, respectively, while the compression modulus slightly decreased. After that, the workers fabricated the IL/PU/PEDOT:PSS composites by sandwiching the IL/PU gel between two conductive polymer films (PEDOT:PSS) as flexible and soft electrodes, which showed excellent bending toward anode.

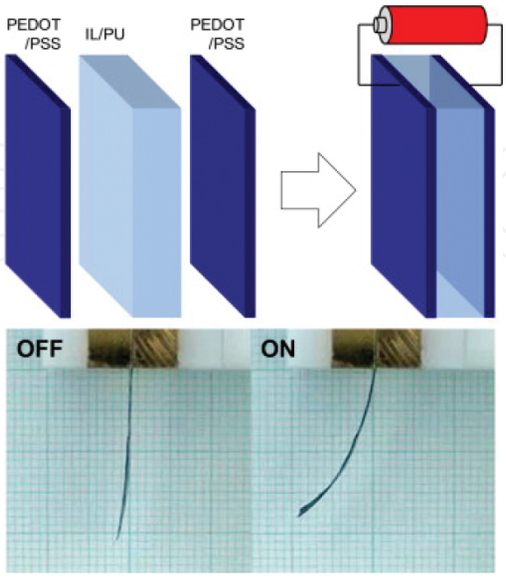

Figure 6. Illustration of IL/PU/PEDOT:PSS composite actuator.

Xia et al. [23] fabricated the molecularly imprinted electrochemical biosensor based on chitosan/ionic liquid-graphene composites modified electrode (CS/IL-GR/GCE) for determination of bovine serum albumin (BSA) (**Figure 7**). The synergistic effects of chitosan, ionic liquid, and graphene nanocomposites improved the electrochemical response and the sensitivity of the sensor. The fabricated sensor possessed a high selectivity, good reproducibility, excellent stability, and acceptable recovery, which indicated the potential application in clinical field.

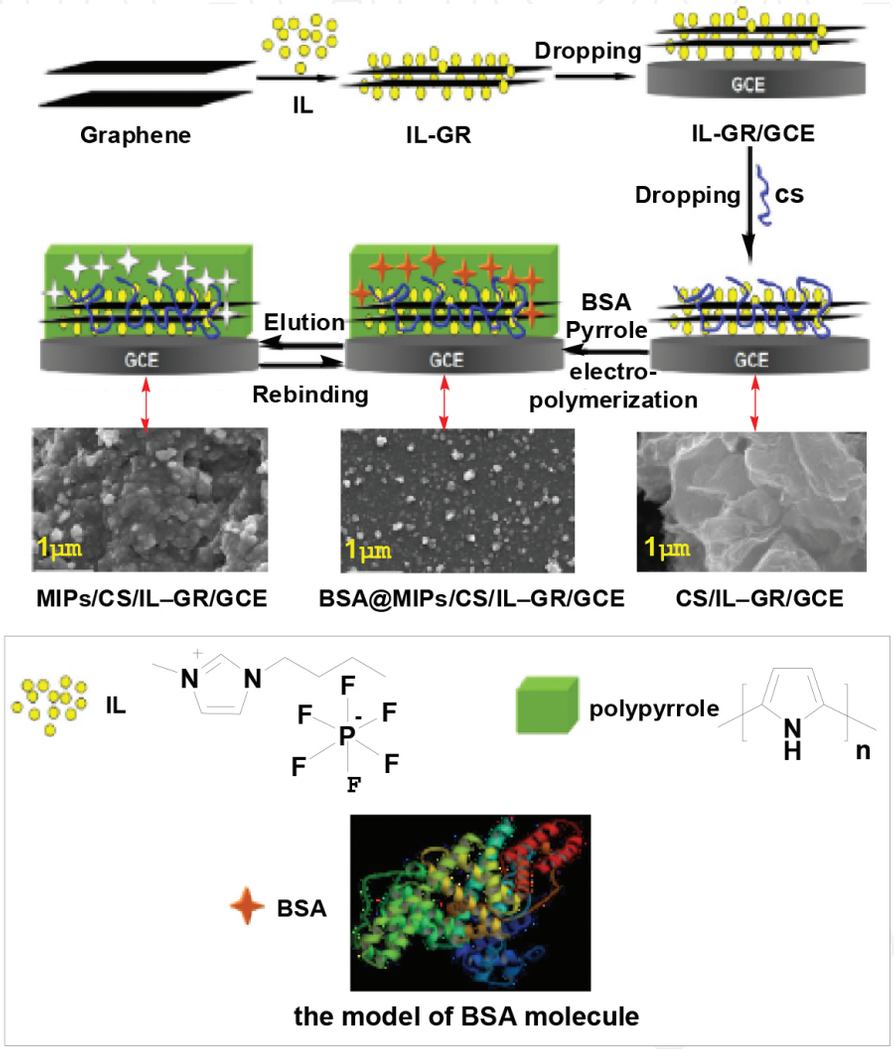

Figure 7. Schematic diagram of the preparation procedure of the molecular imprinted electrochemical sensor.

Zhao and Hao [24] constructed an analytical approach for detecting diaminopyridine derivatives using a molecular imprinting-electrochemical sensor synthesized with 6-aminouracil and 2,6-diaminopyridine (**Figure 8**). Ionic liquid and graphene can assist 2,6-diaminopyridine-imprinted core-shell nanoparticles in electrochemical reaction by increasing conductivity. This proposed method has been demonstrated appropriate sensitivity and selectivity, with a linear range of 0.0500–35.0 mg kg^{-1} and a detection limit as low as 0.0275 mg kg^{-1}.

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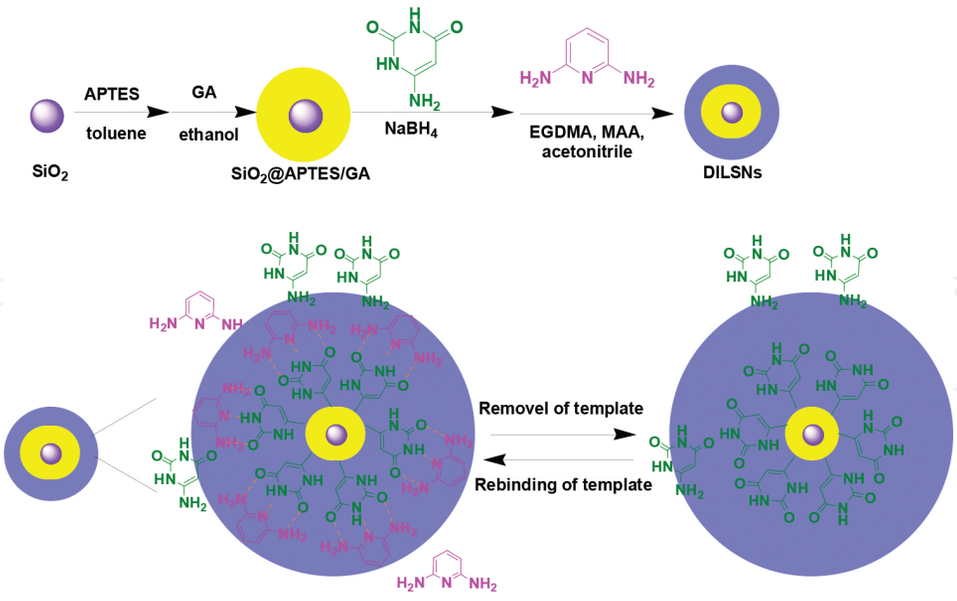

Figure 8. Illustration of the construction of the 2,6-DAP-imprinted core-shell nanoparticles (DICSNs).

Wang et al. [25] synthesized the GNS/Pd nanocomposites by the incorporation of different kinds of ionic liquid (IL) to increase the electrode sensing current toward different analytes (**Figure 9**). They found that BMP-TFSI IL is beneficial for glucose detection, whereas the electrode with BMP-DCA IL shows high sensitivity toward ascorbic acid (AA). Angle-resolved X-ray photoelectron spectroscopy analyses indicate that GNSs can create an aligned cation/anion orientation in the adsorbed IL film, with the anions preferentially occupying the topmost surface. As a result, the electrode sensitivity and selectivity are mainly determined by the IL constituent anions. Chen et al. [26] reported the ultra-sensitive gaseous NH_3 sensor (ECL sensor) based on ionic liquid mediated for directly detecting gaseous NH_3 (**Figure 10**). The NH_3ECL sensor has a very high sensitivity and an excellent selectivity against common interfering gases.

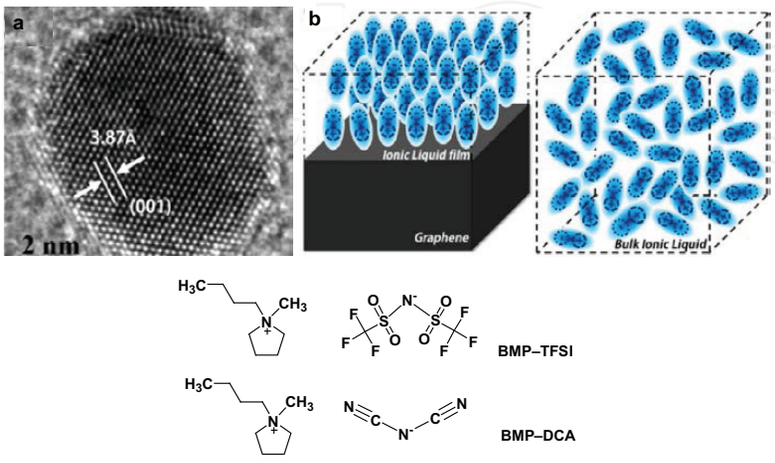

Figure 9. (a) High-resolution TEM micrograph of synthesized Pd nanoparticle means sampling depth is low and (b) schematic of constituent ion orientation in ILs based on different underlying supports.

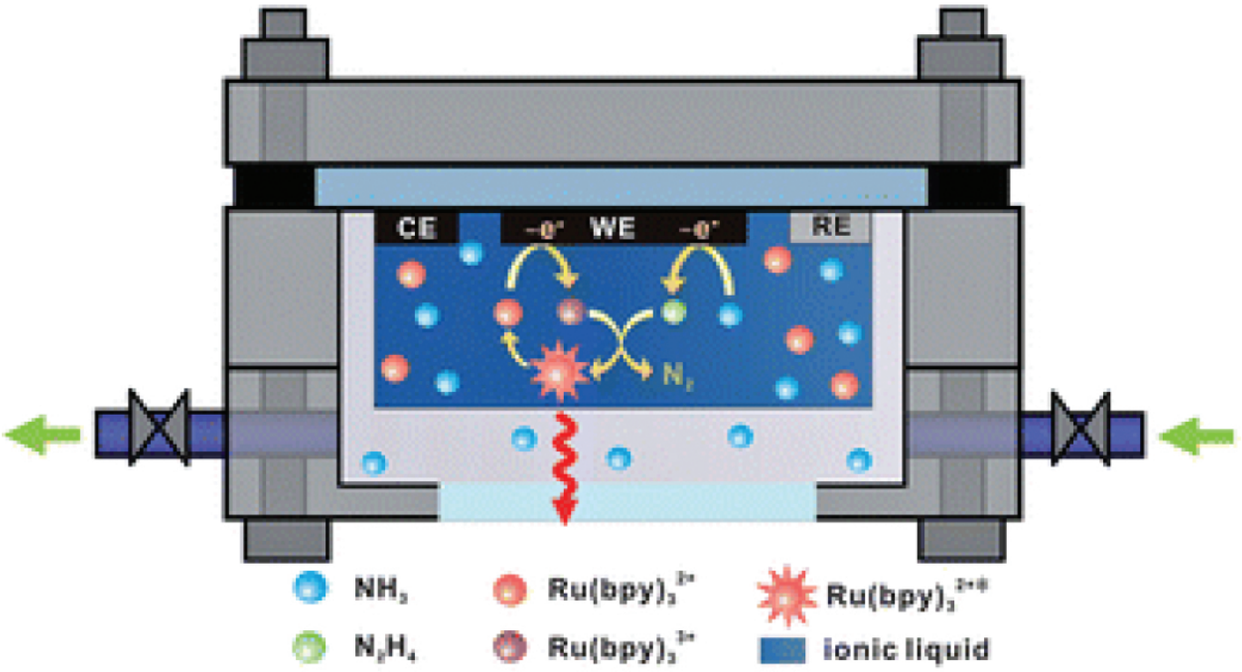

Figure 10. Illustrative ECL sensor for directly detecting gaseous NH_3.

2.2. Electrodeposition

Electrodeposition is an important process, which has been widely applied in industry from functional and decorative anticorrosion to wear-resistant coatings [27]. Aqueous electrolytes are traditionally used in the electrodeposition, and they suffer from limitations such as gas evolution, narrow potential windows, environmental hazards, and necessity for complexing agents [28–30]. Consequently, to overcome these shortcomings, several alternative electrolytes have been developed to substitute for aqueous solvent, although organic solvents have a wider electrochemical potential window; however, their toxicity, volatility, and handling are the major problems for their industrial applications [30]. Ionic liquids (ILs) are green and important electrolytes in electrode position of metals and can circumvent these limitations. Many studies have demonstrated IL electrolytes are favorable for electrode position of nanocrystalline metals, while in aqueous media, pulsed electrode position and addition of additives are required, which often complicates the reaction mechanisms significantly [31].

Suryanto et al. [27] achieved the electrode position of silver onto glassy carbon, gold, and indium tin oxide-coated glass substrates from three room-temperature protic ionic liquids (PILs) (**Figure 11**). The results showed that the electrode position took place through a progressive nucleation and diffusion controlled 3D growth reaction mechanism. The silver micro-/nanoparticles were then employed as electrocatalysts in oxygen reduction reaction and had excellent catalytic activity. This research provided promise for using protic ionic liquids as alternative electrolytes for the electrode position of metals and nanostructured electrocatalysts.

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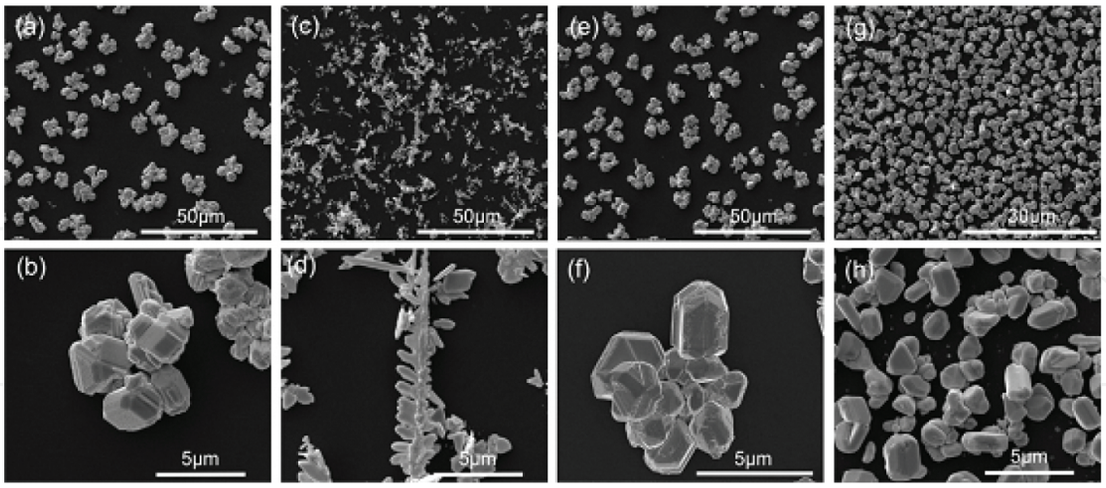
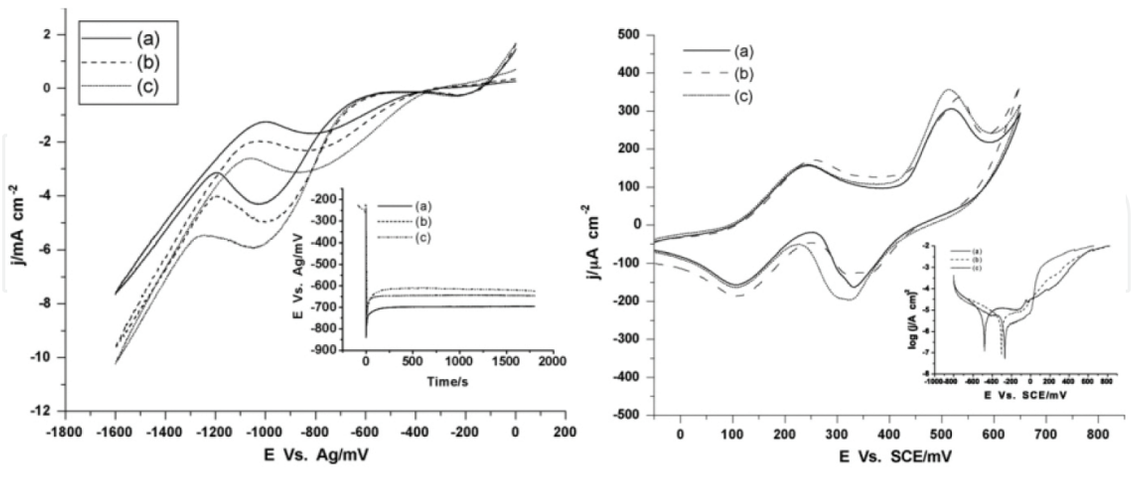


Figure 11. SEM images of silver electrodeposited onto a GC electrode from EAN containing 0.1 M Ag^+ with different deposition parameters. (a and b) Edep = −0.2 V, *t* = 30 s; (c and d) Edep = −0.6 V, *t* = 30 s; (e and f) Edep = −0.2 V, *t* = 60 s; and (g and h) Edep = −0.2 V, *t* = 300 s.

Martis and coworkers [32] investigated the nickel-multiwalled carbon nanotube (Ni/MWCNT) composites electrodeposited in choline chloride/urea-based deep eutectic solvent on a copper substrate (**Figure 12**). Electrodeposition of Ni/MWCNT composites could be easily achieved due to the excellent dispersion stability of MWCNTs in DES nickel chloride solution. Different morphologies and high surface roughness of MWCNTs to the coating were observed through the uniform distribution in the nickel matrix. The results showed that coating with oxygen-functionalized MWCNTs exhibited better corrosion resistance and higher stability than that with pristine MWCNTs.



(A) (B)

Figure 12. A: Cyclic voltammograms for a copper electrode (a) DES + 0.3 M $NiCl_2$, (b) O-MWCNT + 0.3 M $NiCl_2$, and (c) P-MWCNT in DES + 0.3 M $NiCl_2$. SR = 0.02V/s. B: Cyclic voltammograms for (a) bare nickel, (b) Ni/O-MWCNTs, and (c) Ni/P-MWCNTs.

Mascia et al. [33] studied the electrochemical deposition of Cu/Nb composites by using 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide as solvent (**Figure 13**). Structural and chemical analyses indicated that the obtained deposits cover uniformly the electrode surface and exhibit individual layers with a characteristic size ranging between 50 and 100 nm.

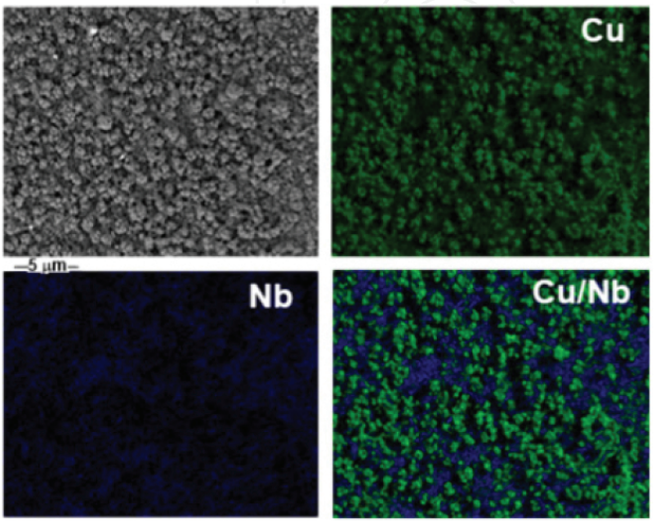


Figure 13. SEM micrograph and elemental maps of the Cu/Nb electrodeposit obtained in dual bathmode: first deposit of copper prepared at −0.75 V for 1800 s, followed by niobium deposit obtained at −1.5 V for 3600 s. The procedure was repeated twice.

Izgorodin et al. [34] synthesized a novel material based on manganese oxide catalyst, which is sensitized and stabilized through a surface phosphorylation reaction in the ionic liquid electrode position reaction (**Figure 14**). The results showed that the surface of the MnOx contained phosphorous at a P/Mn ratio of 1/2, indicating that the surface layer contained phosphate and oxide characteristics. The stability of the catalyst was enhanced and more than 25 h of continuous water oxidation is demonstrated.

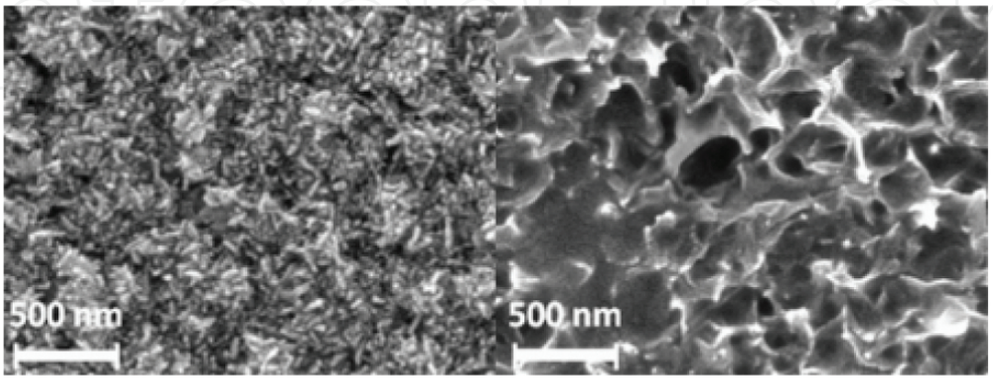


Figure 14. SEM images of the manganese dioxide substrate before (left) and after (right) surface phosphorylation treatment.

Serrà et al. [35] demonstrated a method for grow mesoporous films of Pt-poor alloys (Co_3Pt and $CoPt_3$) through electrode position in ionic liquid-water microemulsions (**Figure 15**). The electrolytic aqueous solution in the IL/W system favors a significant deposition rate. The mesoporous alloys exhibit excellent durability in acidic and alkaline media, maintaining their peculiar morphology, and this prepared catalysts efficient for the methanol electrooxidation in alkaline media.

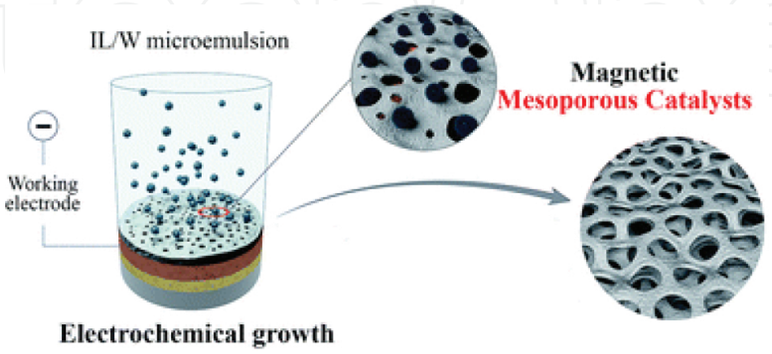


Figure 15. Illustrative approach to grow mesoporous films of Pt-poor alloys (Co_3Pt and $CoPt_3$), based on electrodeposition in ionic liquid-in-water (IL/W) microemulsions.

Bakkar and Neubert [36] conducted the electrode position of aluminum in air, after preparation of ionic liquids in a glove box and covering them by a nonwater-absorbable layer of particular organic compound (**Figure 16**). The functional aluminum layers were successfully deposited from a first-generation ionic liquid $AlCl_3$/[EMIm]Cl (60/40 mol%) on low-carbon steel. SEM/EDX assessments showed that uniform, dense, and adherent Al layers were obtained. Furthermore, adherence of Al to the steel substrate was improved via in situ electrochemical etching.

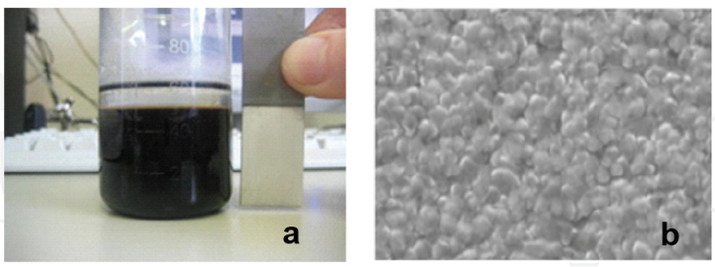


Figure 16. (a) Photograph of a beaker containing $AlCl_3$/[EMIm]Cl ionic liquid insulated from air by a floating layer of decane, in addition to Al electroplated steel strip. (b) SEM micrograph of electrodeposited Al onto low-carbon steel substrate from $AlCl_3$/[EMIm]Cl (60/40 mol%) ionic liquid protected from air by a layer of decane at a potential of −500 mV at ambient atmosphere.

Hekmata et al. [37] arranged the multiwall carbon nanotubes (MWCNTs) in nanochannels of anodic aluminum oxide template (AAO) by electrophoretic deposition (EPD) to make a vertically aligned carbon nanotube (VA-CNT)-based electrode (**Figure 17**). The stabilized CNTs in a water-soluble room-temperature ionic liquid (1-methyl-3-octadecylimidazolium bromide)

were deposited in the pores of AAO templates which were conductive by deposition of Ni nanoparticles in the bottom of pores. The capacitive performance of prepared electrodes was analyzed with a maximum value of 50 Fg^{-1} at the scan rate of 20 mV s^{-1} that was achieved for the specific capacitance.

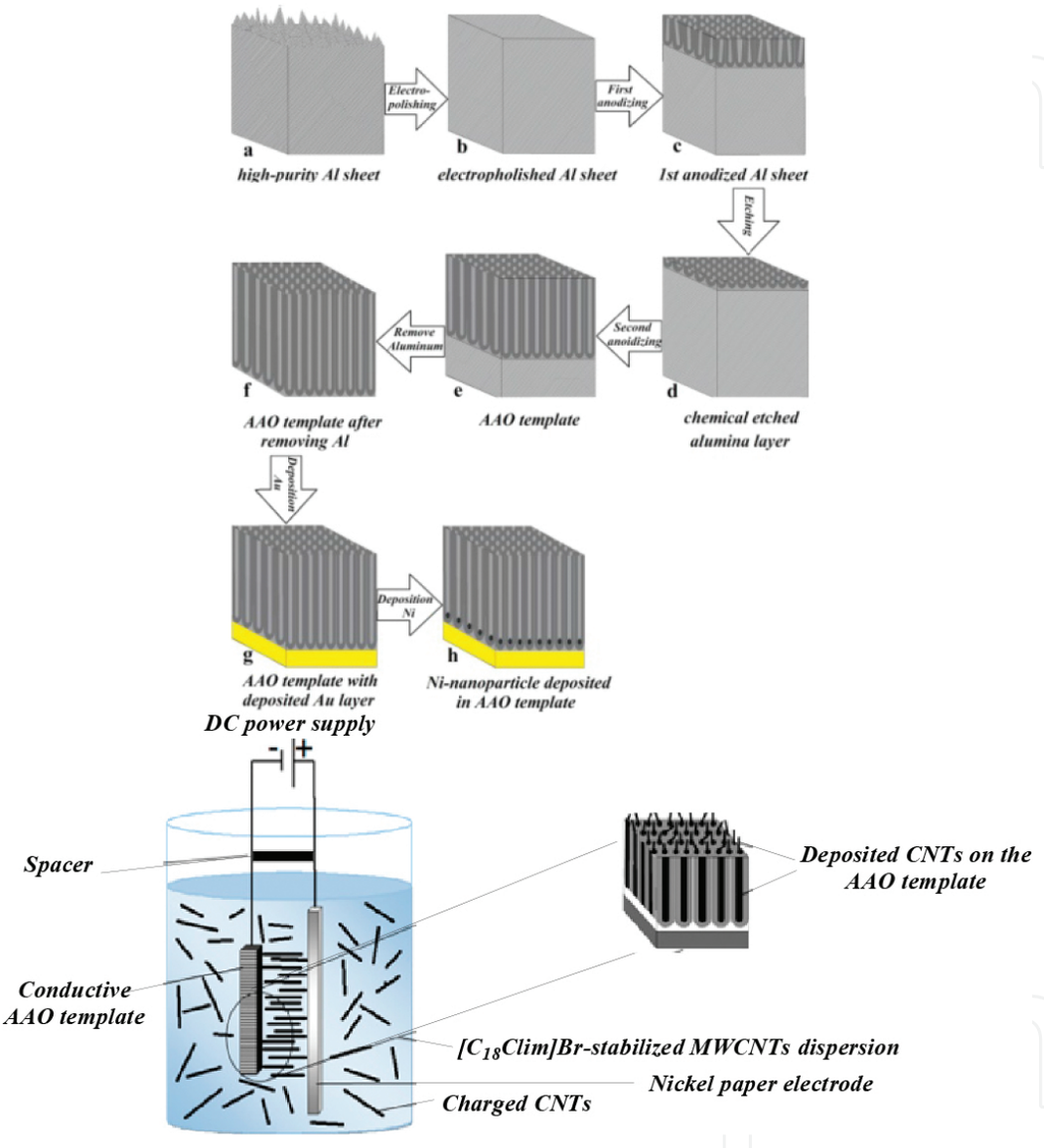


Figure 17. Schematic diagram of an EPD cell for electrophoretic deposition of well-dispersed CNTs on the cathode (as prepared AAO template).

Caporali et al. [38] assessed the feasibility of the use of highly concentrated solutions of ionic liquids to achieve high rates of metal electrodeposition (**Figure 18**). Different ionic liquids containing five transition metals were obtained by dissolving Tf_2N salts of the metals (Ag, Cu, Co, Ni, and zinc) in [bmim][Tf_2N] in a 1:2 molar ratio. The experimental results showed that with the exception of the Ni system, for all the ILs, it was possible to achieve the electroreduction of the metal operating in a normal air atmosphere.

Abebe et al. [39] prepared 4,4-bipyridinium-based ionic liquids which exhibited good metal coordinating abilities and were able to dissolve metal salts at high concentrations (**Figure 19**). The ionic liquid ([C_4Bipyr][Tf_2N]) exhibited a large liquidus range and a wide electrochemical window. Moreover, the successful electrodeposition of Cu (II) to Cu (0) from a solution of $Cu(NO_3)_2$ in [C_4Bipyr][Tf_2N] showed the potential of this new type of ionic liquids for electrodeposition.

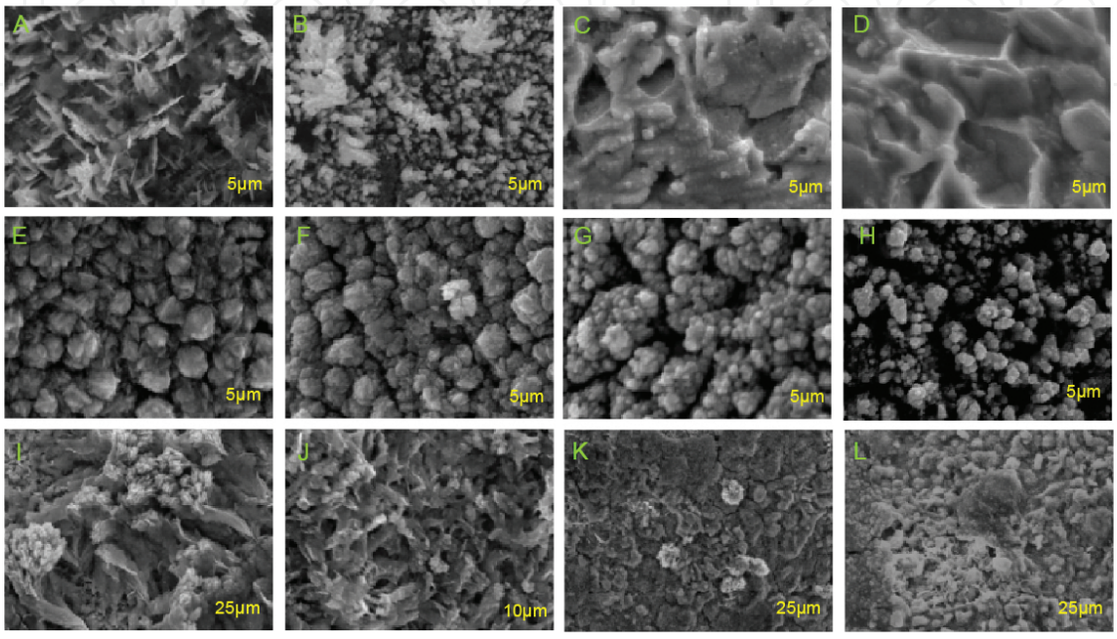


Figure 18. (a) SEM of silver coatings deposited from "wet" (A and B) and "dry" (C and D) AgTf2N:[bmim][Tf2N] 1:2 molar ratio solution. (b) SEM of copper layers deposited from "wet" $Cu(Tf_2N)_2$: [bmim][Tf_2N] 1:2 molar ratio solution as a function of the applied potential. (E) −0.55 V, (F) −0.70 V, (G) −0.85 V, and (H) −0.90 V. (c) SEM of copper layers deposited from "wet" $Co(Tf_2N)_2$: [bmim][Tf_2N] 1:2 molar ratio solution. (I) −1.30 V "dry" solution and (J) −1.30 V "wet" solution. (d) SEM of zinc layers deposited from "wet" $Zn(Tf_2N)_2$: [bmim][Tf_2N] 1:2 molar ratio solution. (K) −1.30 V "dry" solution and (L) −1.30 V "wet" solution.

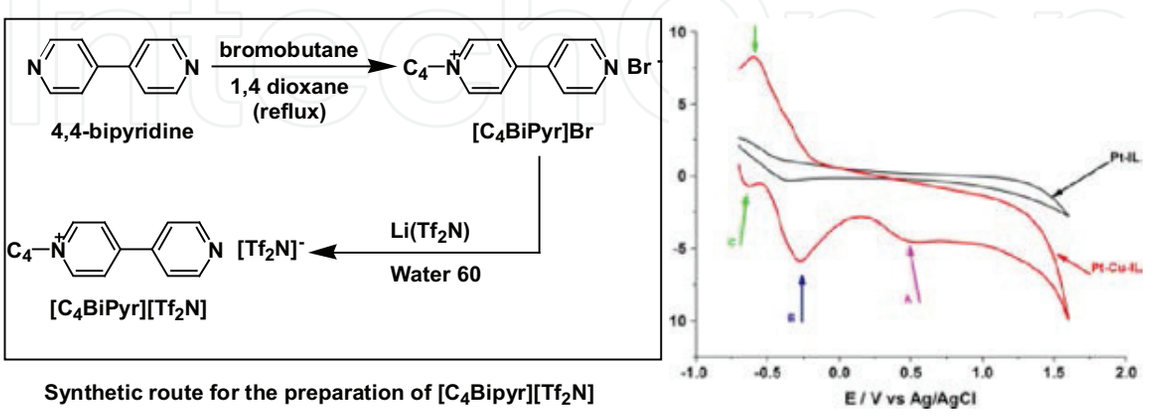


Figure 19. Cyclic voltammogram for the neat [C4Bipyr][Tf2N] (black trace) and the solution of $Cu(NO_3)_2$ in [C4Bipyr][Tf2N] (red trace).

Kosta et al. [40] proposed an electrochemical route to obtain CuI films (**Figure 20**). The approach was based on the electrochemical reduction of I_2 in a solution of copper bis(trifluoromethanesulfonyl)imide salt in 1-butyl-1-methylpyrrolidinium bis(trifluoromethanesulfonyl)imide room-temperature ionic liquid. The mechanisms pointed out that the CuI formation occurred from the chemical reaction between the Cu^{2+} and I^- generated from the I_2 reduction. The researchers also investigated the electrodeposition from organic solvent-based media and found that the solvent nature affected strongly to the nanocrystal packing density. The electrodeposition of ZnO/CuI heterostructures, with high transmittance in the visible range (i.e., >75%), was also reported. The current density-voltage characteristic of the resulting device exhibited clear rectifying behavior with a rectification of ~ 2×10^3 at $V = \pm 1.5$ V.

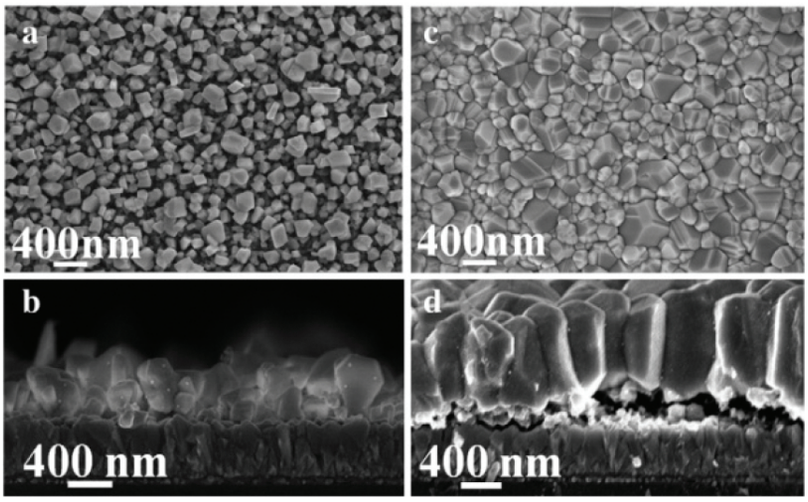


Figure 20. FESEM micrographs of the top view and cross section of films obtained from PYR14TFSI (a and b) and isopropanol (c and d)-based media.

2.3. Electroredox

Mourada et al. [41] described the biredox ionic liquid electrolytes in which both anion and cation are functionalized with anthraquinone and 2,2,6,6-tetramethylpiperidinyl-1-oxyl (TEMPO) groups, respectively (**Figure 21**). At the same time, they carried out the in-depth investigations based on crossed experimental and theoretical studies to elucidate how the bulkiness of ions bearing a redox moiety impacted electron and mass transfers and accordingly the efficiency of electrochemical devices. In such redox species, the electron transfer was not governed by the overall size of the solvated redox species, which took preferential orientation toward the surface.

Yoo et al. [42] investigated the electrical performance of a Li-air cell with ionic liquid electrolytes operating at high temperature. A continuum-based model was used to quantify the performance of the Li-air cell, with an ionic liquid (MPPY-TFSI) electrolyte as a function of operating temperature (**Figure 22**). The molecular dynamics (MD) simulations indicated that oxygen solubility in ionic liquid increases with temperature, which is very favorable for high-

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temperature operation. The continuum-based cell level simulation results showed that the battery performance can be improved significantly by increasing operating temperature. Simulation results also revealed that by increasing the operating temperature, the specific capacity can be improved significantly for high load current density. They also investigated the effect of different temperatures on the performance of Li-air battery, and the results showed that the transport limitation of oxygen and lithium ions could be alleviated at higher temperatures.

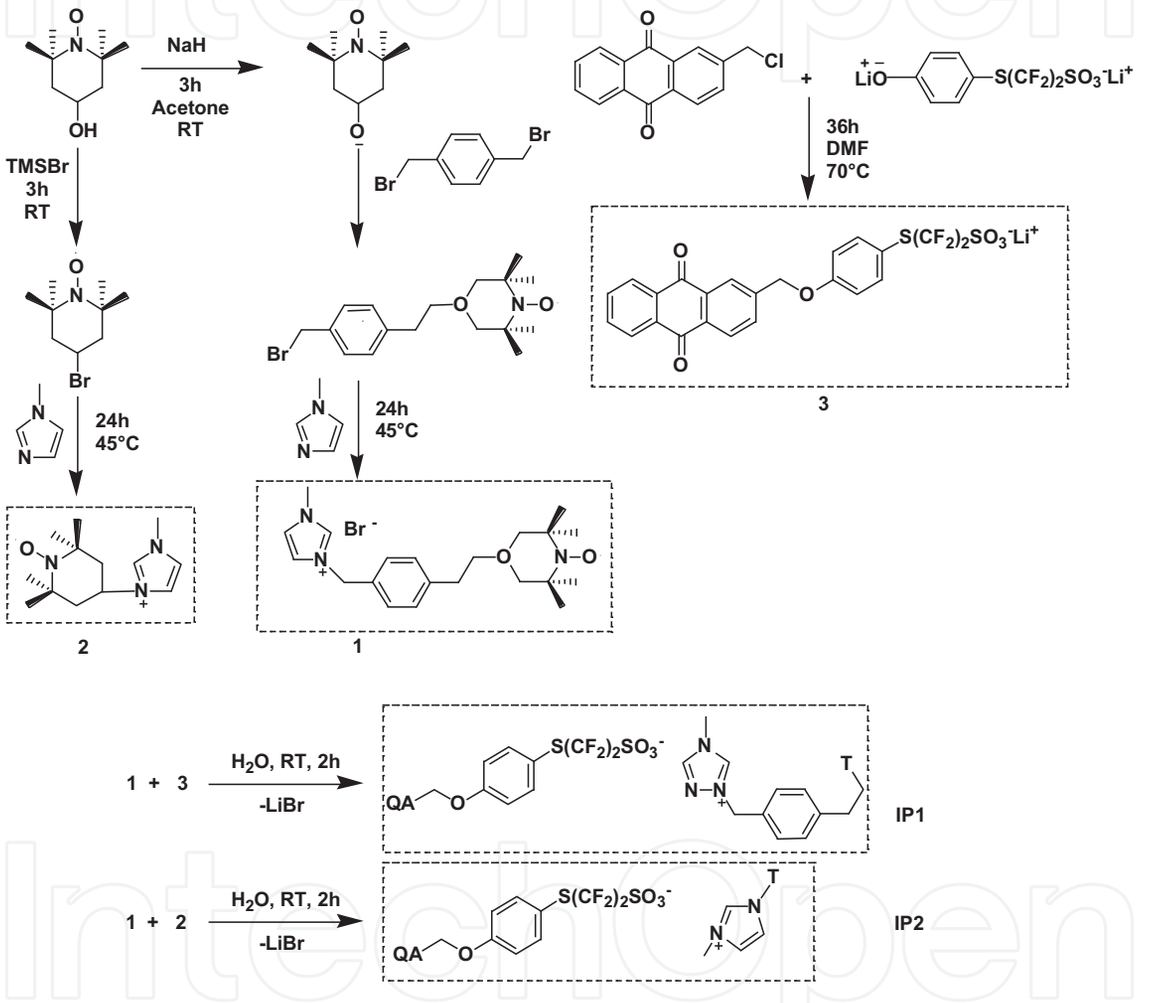

Figure 21. Synthesis route to obtain redox cationic and anionic species for the biredox ILs named IP1 and IP2. AQ and T denote the anthraquinone and TEMPO moiety, respectively.

Ueda et al. [43] investigated the electrochemical stability of a fullerene (C_{60}) thin film supported on Au(1 1 1) in an ionic liquid electrolyte [C4mpyrr][Tf2N] (**Figure 23**). The obtained result indicated that the dissolution of the C_{60} film was caused by cation insertion and accelerated by the generation of multiple redox states of C_{60}^{n-} $(n = 1 - 6)$ during the continuous scans. The redox states of C_{60} in [C_4mpyrr][Tf_2N] could be clearly controlled by the scan rate and temperature.

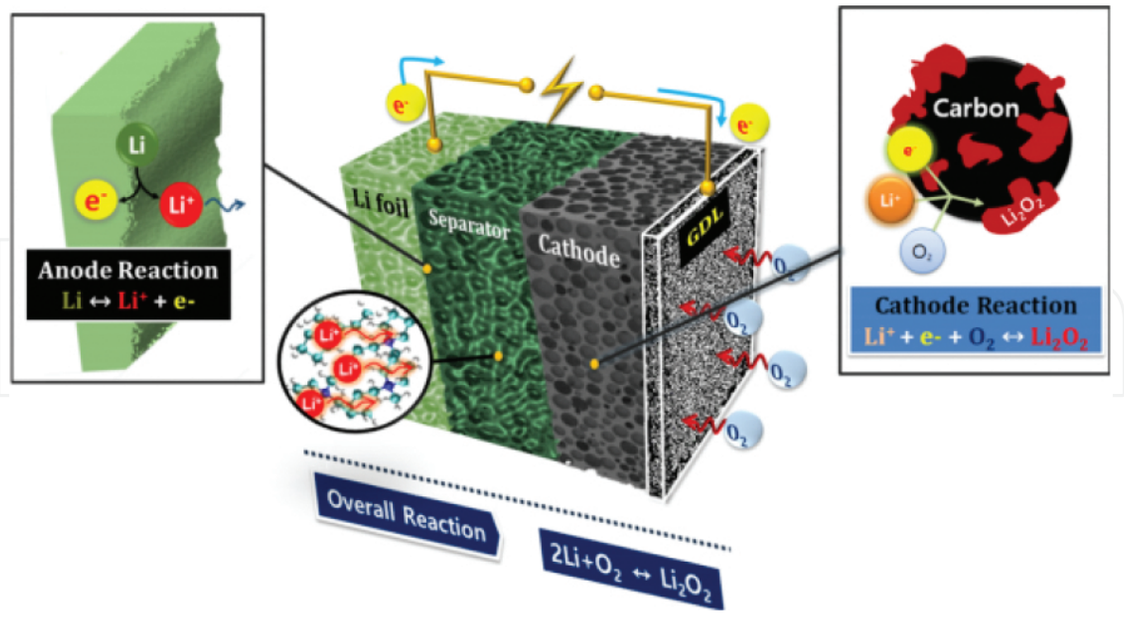

Figure 22. Illustration of Li-air battery with corresponding electrochemical reactions at anode and cathode side.

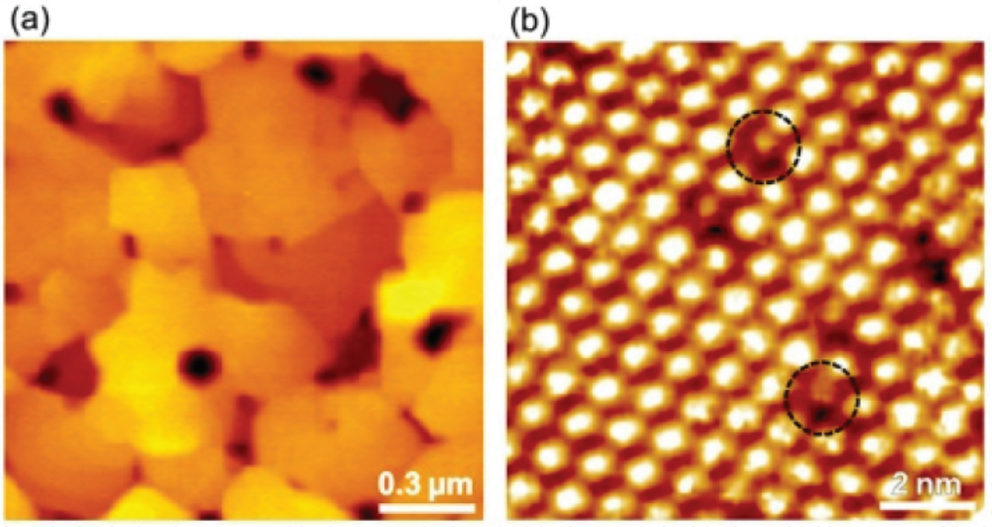

Figure 23. (a) AFM image (1.5 × 1.5 μm^2) and (b) high-resolution STM image (10 × 10 nm^2) of C_{60}-deposited Au/mica surface. Note that STM image was obtained under electrochemical condition in 0.1 M $HClO_4$.

Sonkaria et al. [44] carried out the ionic liquid-induced synthesis of a graphene intercalated ferrocene nanocatalyst (**Figure 24**), which was the first demonstration approach for the assembly of ferrocene in ionic liquids. Hooshyari et al. [45] prepared two types of innovative composite membranes based on polybenzimidazole (PBI) containing dicationic ionic liquid PDC_3 and monocationic ionic liquid PMC_6 as electrolyte for high-temperature fuel cell applications under anhydrous conditions (**Figure 25**). The analyses of results displayed high proton conductivity and thermal stability. Moreover, the fuel cell performance of PA doped PDC_3 composite membranes was enhanced at high temperatures.

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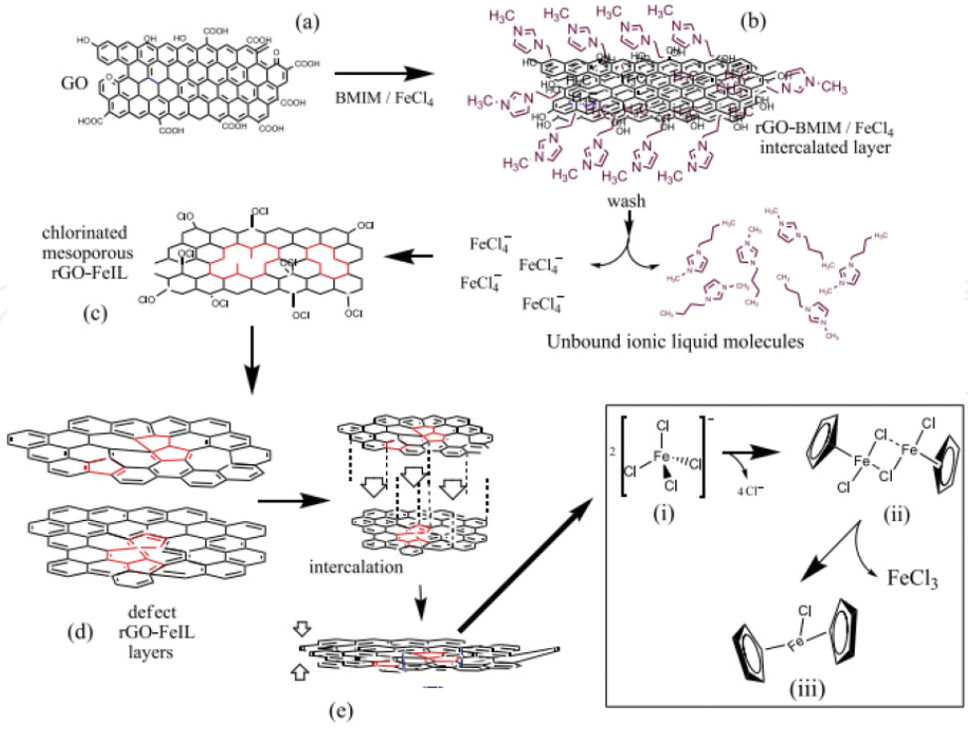

Figure 24. Chemical events between rGO and FeIL leading to the intercalation of Fe at defect positions (shown in red) stabilized by a ferrocene/ferrocenyl configuration.

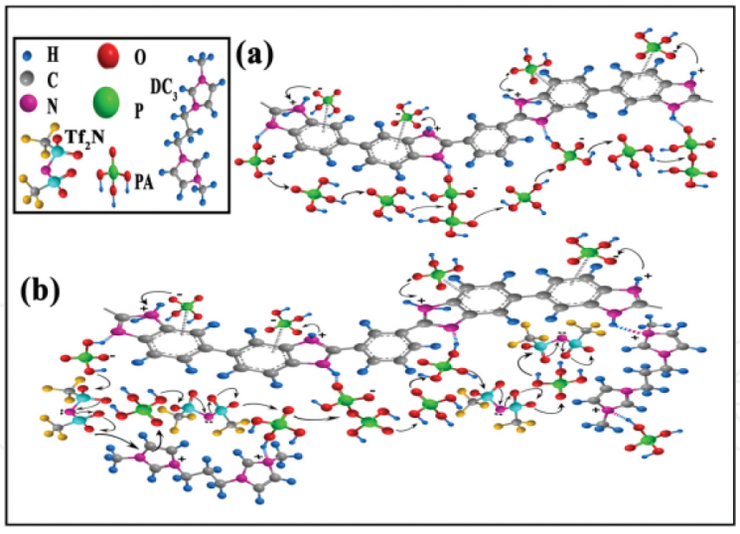

Figure 25. Schemes of the proton transport mechanism for (a) PA-PBI and (b) $PPDC_{3X}$ membranes.

Ueda et al. [46] investigated the control of the redox states of highly charged C_{60} anions in two ionic liquids (ILs) (**Figure 26**). The results showed that highly charged reduced states of C_{60}^{5-} and C_{60}^{6-} could be produced and detected at room temperature by using an electrochemical interface between a multilayered C_{60} adlayer on a Au(1 1 1) electrode and N-butyl-N-methyl-

pyrrolidinium-based IL, whereas a tributylmethylammonium-based IL provided less than four redox waves of C_{60}. The results of the present study suggested that both a wide potential window and the interaction between C_{60} anions and IL cations are important for controlling the multiple redox states of C_{60} at room temperature.

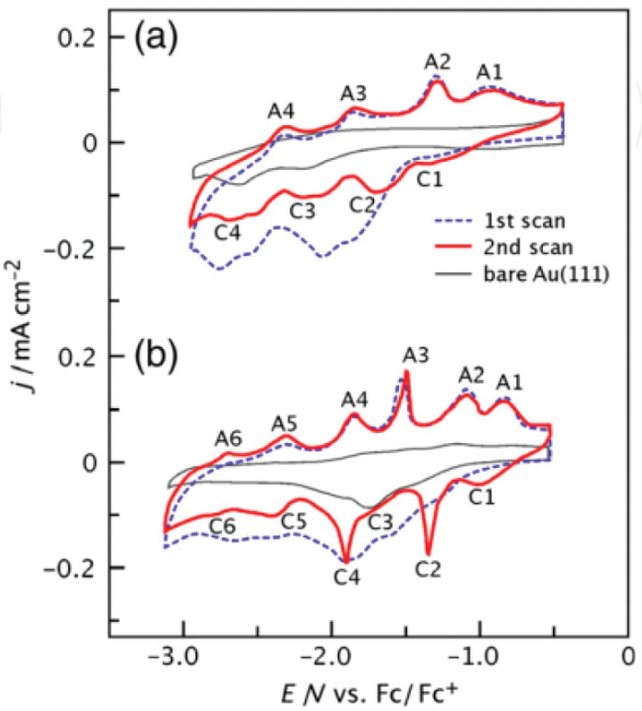

Figure 26. Typical cyclic voltammograms of a clean Au(1 1 1) electrode (gray line) and a C_{60}-modified Au(1 1 1) electrode obtained in $[TFSI]^-$-based ILs with (a) $[N_{1,4,4,4}]^+$ and (b) $[C_4mpyrr]^+$, respectively, at 25 °C. The blue dotted and red solid lines indicate the first and second scans, respectively, of the C_{60}-modified Au(1 1 1) single-crystal electrode. The scan rate was 0.5 V s^{-1}.

Fu et al. [47] presented a spontaneous vertical phase separation (SVPS) self-assembled bilayers structure with BenMeIm-Cl ionic liquid (IL) interfacial bottom layer and a photoactive top layer via a single spin-coated step of BenMeIm-Cl IL and organic donor-acceptor composite and achieved a PCE as high as 8% based on IPSCs with PTB7 as the donor (**Figure 27**). The presence of BenMeIm-Cl IL reduced the work function of ITO and led to a better energy-level matching for efficient charge transfer. The driving force of SVPS self-assembled structure was from the relative surface energy difference between organic materials and BenMeIm-Cl ILs, together with their interactions with the substrates. This self-assembled process procedure paved the way to simplify the manufacturing of low-cost and large-area organic electronic devices. Chen et al. [48] studied the metal binary sulfides (TiS_2, FeS_2), in either powder or thin film forms, Li insertion electrodes for rechargeable lithium batteries. They exploited the equilibrium solubility of molecular sulfur into ionic liquids at its melting point (120°C), to prepare thin films of both Co_9S_8 and FeS_x (**Figure 28**). The researchers demonstrated that the growth of Co_9S_8 films involved the reaction of soluble sulfur with the electrodeposited Co metallic layer.

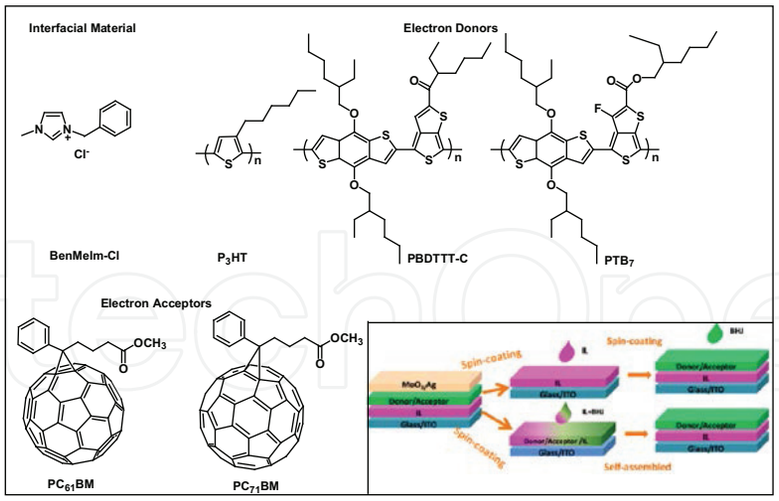

Figure 27. Chemical structures of BenMeIm-Cl IL and BHJ materials.

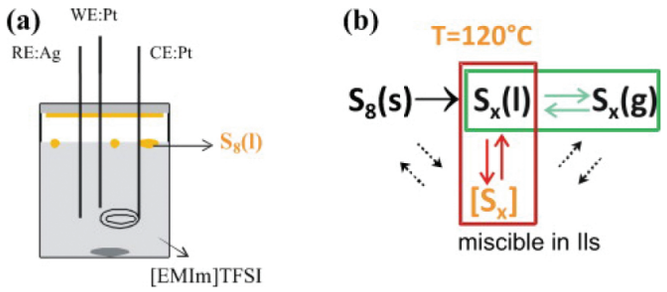

Figure 28. (a) Schematic setup of sulfur in the electrochemical cell and (b) possible equilibriums of different phases of sulfur in [EMIm]TFSI.

2.4. Other applications

Viaua et al. [49] studied the electropolymerization of pyrrole films in three room-temperature ionic liquids: bmim-PF_6, emim-TFSA, and bmp-TFSA (**Figure 29**). The experimental results showed that the difference of activity from one polymer film to the other was mainly attributed to the difference of viscosity between the solvents used. Li et al. [50] prepared the composite films of poly(3,4-ethylenedioxythiophene) (PEDOT) doped with various functional ionic liquids by electropolymerization process on indium-doped tin oxide (ITO) conducting glasses (**Figure 30**). The ITO glasses coated with the composite films were used as the counter electrodes in dye-sensitized solar cells, and various imidazolium cations with different alkyl chains and anions were used as the ionic liquids. Palombi et al. [51] investigated the double electrosynthesis of 3-((4S)-benzyl-2-oxo-oxazolidin-3-carbonyl)-heptane-2,6-dione (2a) at the cathodic and anodic compartments of a divided glass cell in ionic liquid [Emim]BF_4 (**Figure 31**). In this electrolysis, ionic liquid played the role of solvent/electrolyte system for the cathodically initiated reaction and electrolyte/pre-catalyst for the anodic one. Dong et al. [52] synthesized the monodisperse poly(ionic liquid) particles for use as high-performance

anhydrous polyelectrolyte-based smart electrorheological materials (**Figure 32**). The results showed that the ionic liquid particles possessed strong electrorheological effect in dry state and the electrorheological effect depended on the size of cation/anion parts.

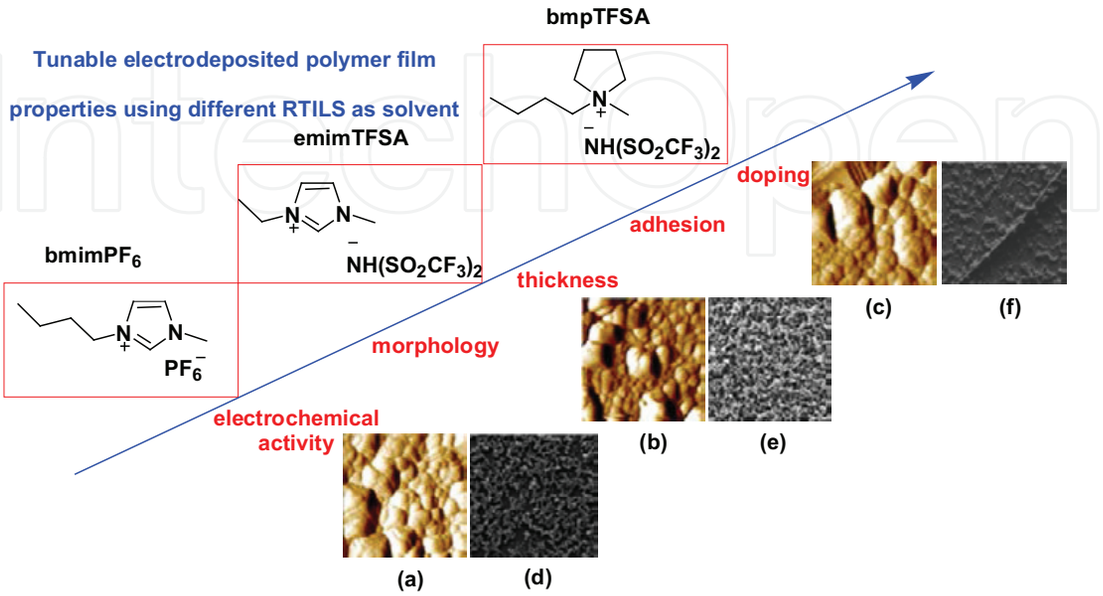

Figure 29. AFM images of PPy-bmim-PF6 (a), PPy-emim-TFSA (b), and PPy-bmp-TFSA (c). SEM images of PPy-bmim-PF6 (d), PPy-emim-TFSA (e), and PPy-bmp-TFSA (f).

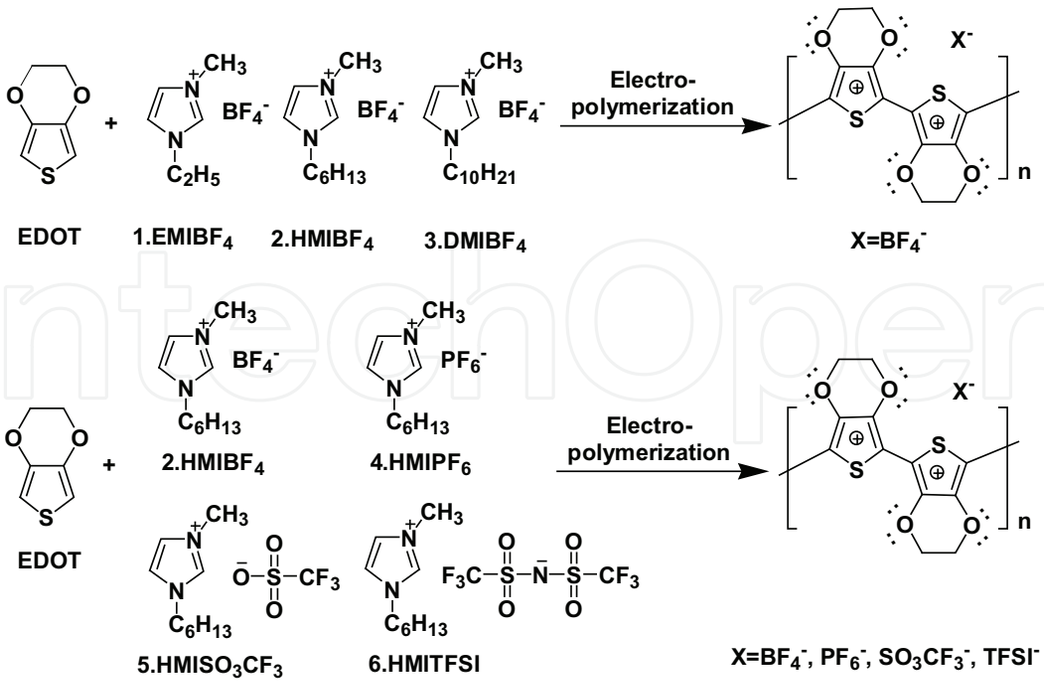

Figure 30. Illustrative electropolymerization process for the PEDOT counter electrodes (a) doped with various alkyl chains in imidazolium cations and (b) doped with different anions.

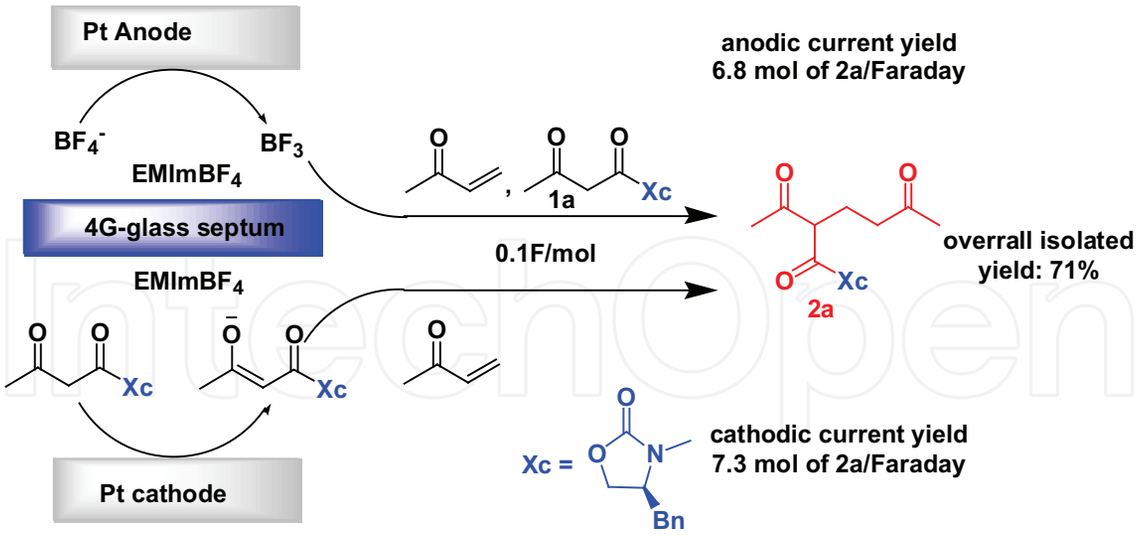

Figure 31. Synthesis of Michael adduct 2a by paired electrolysis in BF_4-based ionic liquid.

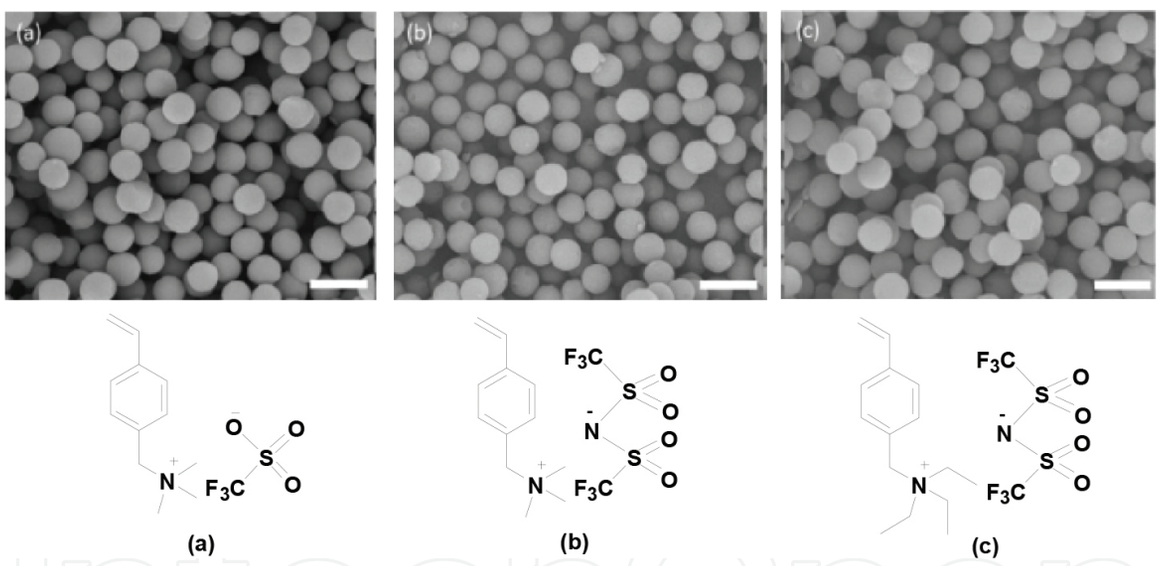

Figure 32. The SEM images of PIL particles: (a) poly(VBTMA$^+CF_3SO_3^-$), (b) poly (VBTMA$^+(CF_3SO_2)_2N^-$), and (c) poly(VBTEA$^+(CF_3SO_2)_2N^-$).

Kaminski et al. [53] presented an innovative methodology for a liquid-liquid extraction process based on an electrically induced emulsion of ionic liquid 1-[bmim][$MeSO_4$] as the extracting solvent dispersed in an organic mixture (**Figure 33**), and this liquid-liquid extraction provided an environmentally friendly process as an alternative to azeotropic distillation. Martínez et al. [54] studied the performance of terracotta separators modified with the same ionic liquid [Emim][NTf_2], neat, and also mixed with PTFE binder (**Figure 34**). They found the operational limitations when the IL was integrated in the ceramic separator, there was a significant enhancement of the MFC performance when added as part of the activated layer mixture of the cathode. Najafabadi and Gyenge [55] reported the simultaneous anodic and cathodic GN

production in two types of electrochemical cells in aprotic ionic liquid electrolytes (**Figure 35**). They demonstrated a synergistic exfoliation effect when the iso-molded graphite anode and cathode were subjected to a constant cell potential, generating up to three times higher exfoliation yields than single electrode studied on each side.

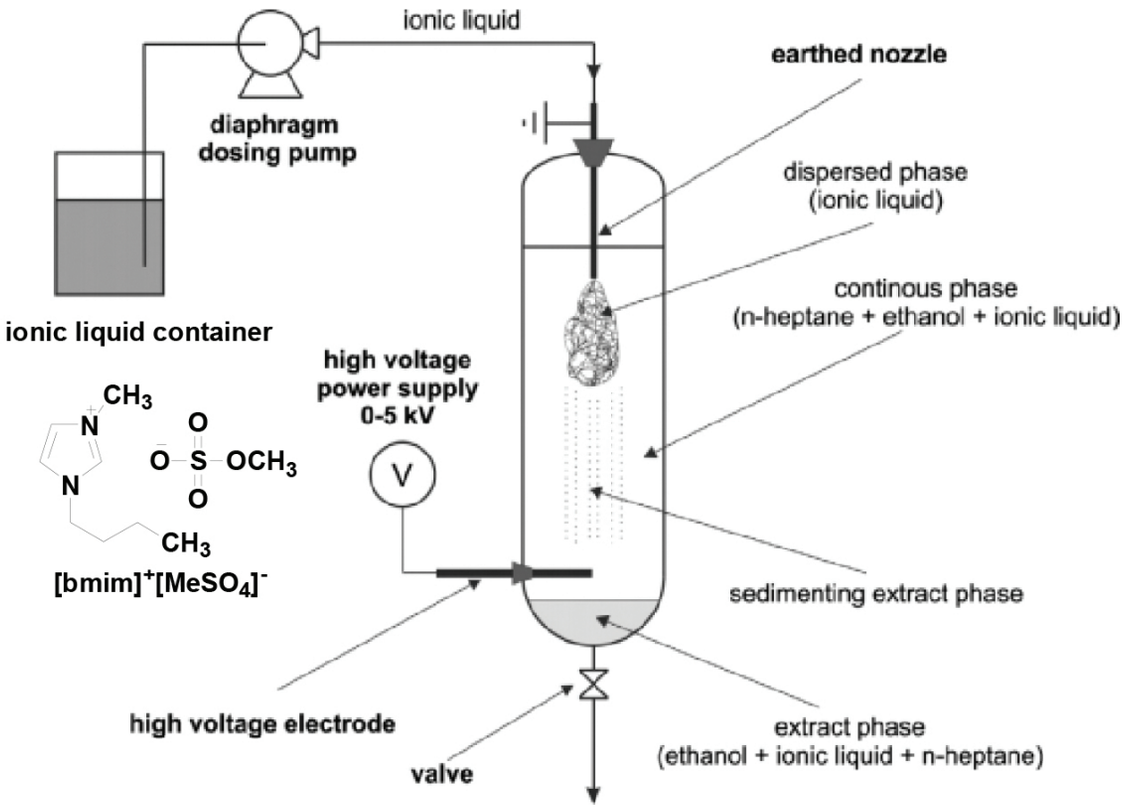

Figure 33. Scheme of the general experimental arrangement.

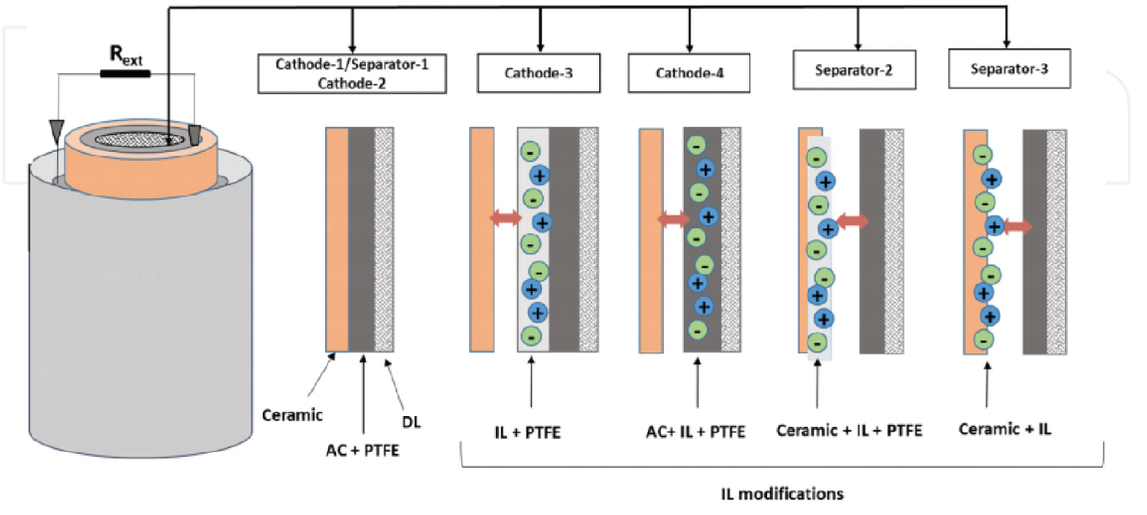

Figure 34. Configuration of the cathodes and the separators.

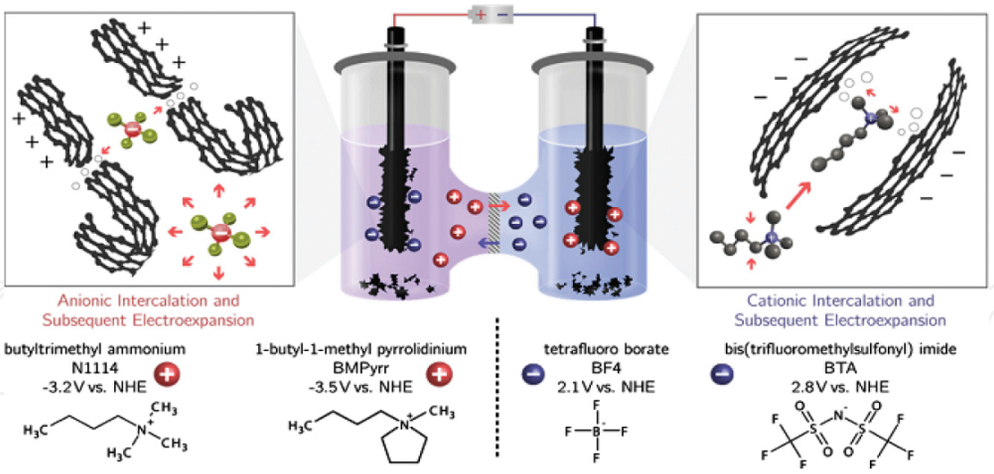

Figure 35. Electro-exfoliation of graphitic anodes and cathodes in ionic liquids.

3. Conclusions

In summary, a remarkable amount of progress has been made in recent years in the field of electrocatalysis in the presence of ionic liquids. Despite the impressive progress, a number of challenges still remain: the current studies mainly focus on the applications of ILs while lacking of systematicness in its theoretical research. There is absolutely a need for the search of inherent structures, purity, distribution, and orientation of ILs at electrode interface. We do believe that ionic liquids as a green solvent, which is expected to replace the water, organic solvents, and molten salt, will play a greater role in electrocatalytic system.

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